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SHORT COMMUNICATION

Reactions of organoaluminium compounds with benzyl cyanide

In our previous studies, the IR spectra and reactions of organoaluminium compounds with nitriles, particularly benzonitrile, were investigated[1-4]. Some reactions of nitriles with organoaluminium compounds have been described by Reinheckel and Jahnke[5] and Wade *et al.*[6,7].

In the present study, the reactions of organoaluminium compounds with benzyl cyanide have been investigated to determine the effect of the mobile hydrogen in the position alpha to the triple bond, on the reaction course. Characteristic bands in the IR spectra were followed during the reaction and the data are listed in Table 1.

TABLE 1

REACTION COURSE OF BENZYL CYANIDE WITH TRIMETHYLALUMINIUM AND DIMETHYLALUMINIUM CHLORIDE IN XYLENE AT 135°. CHANGES OF CHARACTERISTIC BANDS IN INFRARED SPECTRA
Intensity signs: v, very; s, strong; m, medium; w, weak; sh, shoulder.

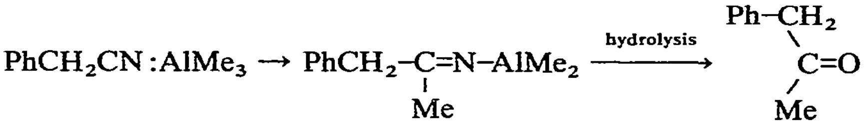
Reaction time (h)	$PhCH_2CN\cdot Me_3Al$						
	1:1				1:4		
	$\nu(C\equiv N)_k$	$\nu(C=C=N)$		$\nu(C=N)$	$\nu(C\equiv N)_k$	$\nu(C=C=N)$	$\nu(C=N)$
0	2305 vs				2305 vs		
0.5	2305 m	2140 w	2020 m	1665 vs	2305 m		1665 s
1	2305 vw	2140 w	2020 m	1665 vs	2305 vw		1665 vs
2	not investigated				not investigated		
3		2140 w	2020 vw	1665 vs			1665 vs
4	not investigated				not investigated		
6		2140 vw		1665 vs	not investigated		
8	not investigated				not investigated		

Reaction time (h)	$PhCH_2CN\cdot Me_2AlCl$							
	1:1				1:2			
	$\nu(C\equiv N)_k$	$\nu(C=C=N)$		$\nu(C=N)$	$\nu(C\equiv N)_k$	$\nu(C=C=N)$		$\nu(C=N)$
0	2309 vs				2309 vs			
0.5	not investigated				not investigated			
1	2309 vs	2185 w		1645 m	2309 s	2185 vw		1645 m
2	2309 vs	2185 m	1720 sh	1665 sh 1645 m 1620 sh	2309 s	2185 m		1645 s
3	not investigated				not investigated			
4	2309 s	2185 s	1720 mw	1645 s 1620 sh	2309 ms	2185 vs	1665 s	1645 s 1620 sh
6	2309 m	2185 s	1720 mw	1645 vs 1630 sh	2309 mw	2185 vs	1665 s	
8	not investigated				2309 vw	2185 vs	1665 sh	1645 vs 1620 sh

A comparison of the characteristic band intensities of the reactants and products indicates the direction and rate of the reaction, and the data obtained show that both depend on the nature of the organoaluminium compound and the molar ratio of the reactants.

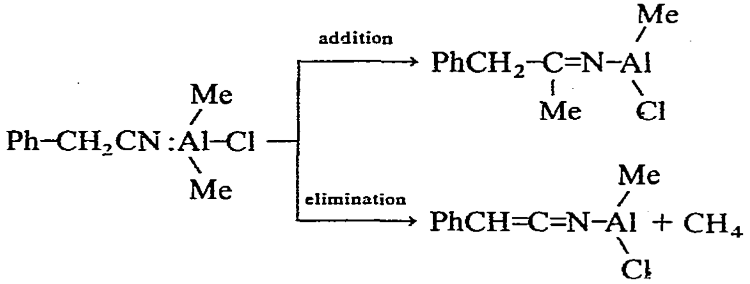
Trimethylaluminium reacts much more rapidly (about 10 times) with benzyl cyanide than does dimethylaluminium chloride. This can be deduced from an intensity decrease in the $\nu(C{\equiv}N)$ band of the complex and an increase in the corresponding $\nu(C{=}N)$ and $\nu(C{=}C{=}N)$ bands of the products.

The reaction produces mainly a ketimine derivative; upon hydrolysis, the corresponding ketone is formed



$$PhCH_2CN:AlMe_3 \rightarrow PhCH_2\underset{\large Me}{\underset{|}{C}}{=}N{-}AlMe_2 \xrightarrow{\text{hydrolysis}} \begin{matrix} Ph{-}CH_2 \\ \diagdown \\ C{=}O \\ / \\ Me \end{matrix}$$

The reaction of dimethylaluminium chloride is much slower and proceeds simultaneously in two directions:



$$\begin{matrix} Me \\ / \\ Ph{-}CH_2CN:Al{-}Cl \\ \diagdown \\ Me \end{matrix} \begin{cases} \xrightarrow{\text{addition}} PhCH_2{-}\underset{Me}{\underset{|}{C}}{=}N{-}Al\begin{matrix} Me \\ Cl \end{matrix} \\ \xrightarrow{\text{elimination}} PhCH{=}C{=}N{-}Al\begin{matrix} Me \\ Cl \end{matrix} + CH_4 \end{cases}$$

This hypothesis is supported by two new and strong absorption bands: one at 2185 cm^{-1} assumed to be due to the $-C{=}C{=}N$ system of coupled bonds, and the other at 1645 cm^{-1} resulting from absorption by the $-C{=}N-$ grouping of the ketimine. When the ratio was changed (using an excess of the organoaluminium compound) the overall reaction rate and, particularly, the velocity of the addition reaction, were increased.

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